IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appl. No	:	10/596,489	Confirmation No.	:	7292
Applicant	:	Abdur-Rashid, Kamaluddin			
Filed	:	December 15, 2004			
Title	:	Asymmetric Imine Hydrogenation Processes			
TC./A.U.	:	1621			
Examiner	:	Nwaonicha, Chukwuma O			
Docket No.	:	14696-13			

Honorable Commissioner for Patents
P. O. Box 1450
Alexandria, Virginia 22313–1450

Dear Sir:

DECLARATION UNDER 37 CFR §1.132

I, Kamaluddin Abdur-Rashid, a citizen of Canada, and resident of Mississauga, Ontario, Canada, declare that the following facts are within my knowledge and are true.

1. I reside at 3414 Joan Drive, Mississauga, Ontario, Canada L5B 1T5.

2. I am the inventor and owner of the subject matter as claimed in U.S. Patent Application No. 10/596,489 filed December 15, 2004 (hereafter "the Application").

3. I have read and understood the Office Action that issued for the Application on August 3, 2009. The Examiner is of the view that claims 1, 3, 5-15, 16-19 and 25-53 are obvious in light of Cobley et al. (US 6,528,687) in view of Abdur-Rashid (WO 03/097571).

4. I herein enclose photocopied pages of my laboratory notebook containing pages 1-70. I submit that this notebook contains experimental data which forms the basis for the subject matter of the claims of the Application. I note that the

notebook also contains experimental data that is not related to the subject matter of the Application.

5. I respectfully submit that the first day on which an imine falling within the scope of formula I in the Application was successfully hydrogenated using the process of the Application, is after the date on which Abdur-Rashid was assigned to myself. I note that this experiment is found on page 52 of my notebook.

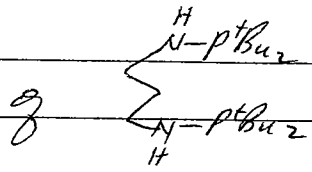
6. I therefore submit that the date the present invention was made is after the date of assignment of the prior art reference Abdur-Rashid to myself.

7. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statement and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the Application or patent resulting therefrom.

October 30, 2009
Date

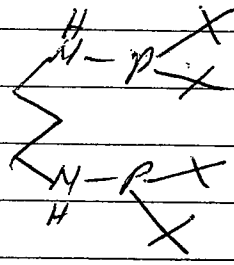
Kamaluddin Abdur-Rashid

[redacted]

Preparation of 

A solution of 1,3-diaminopropane (3.72g, 50 mmol) in toluene (25 ml) was added dropwise to a solution of di-tert-Butylphinous chloride (9.03g, 50 mmol) in 50 ml toluene. The mixture was refluxed for 4 hours under argon. The ammonium chloride salt was removed by filtration through a sintered glass frit. The solvent was removed under vacuum and the product purified by distillation under vacuum.

yield = 6.62g



PNCNP

02

[redacted] Reaction of $RuCl_2(p\text{-cymene})$ + PNCNP

A mixture of 15mg $RuCl_2(p\text{-cymene})$ and PNCNP (18mg) and NEt_3 (10mg) was refluxed in 0.6g of ^tBuOH. The NMR spectrum showed the formation of two isomers of the olefin complex, the alkylidene complex + a degradation compound? There was some degradation of the ligand to generate a broad singlet at δ 152.1
NB- No reaction at room temperature

[redacted] A mixture of $RuCl_2(p\text{-cymene})$ (15mg), PNCNP (18mg) and NEt_3 (10mg) and ^iPrOH (1 drop) was heated to 110°C in toluene (0.6g) The NMR showed the formation of the olefin isomers, the alkylidene complex, ~~and~~ and several degradation compounds, including byproduct of the ligand.

[redacted] A mixture of $(RuCl_2(COD))_n$ (15mg), PNCNP (18mg), NEt_3 and ^iPrOH (1 drop) was warmed at 60°C in toluene for several hours. The NMR spectrum showed the formation of the above-mentioned products in addition to degradation species.

[redacted]

Reaction of $RuCl_2$(p-cymene) + PNCNP

A mixture of $RuCl_2$(p-cymene) (15mg), PNCNP (18mg) and lutidine (10mg) was warmed at 60°C in toluene. The NMR spectra of the mixture showed the formation of the olefin isomers, alkylidene and [redacted] unknown compound. The mixture was refluxed overnight. Several degradation products was observed by NMR.

A mixture of $RuCl_2$(p-cymene) (15mg), PNCNP (18mg), lutidine (10mg) was warmed at 60°C in BuOH (0.6g). The NMR spectra showed the gradual formation of the olefins, alkylidene and unknown compound. The mixture was heated at 80°C overnight. The NMR spectrum showed the new compound as the main product. It seems to relatively insoluble. The mixture was filtered, washed with 1ml methanol and dried. The solids were collected in CD_2Cl_2 (sparingly soluble). The NMR spectrum showed this as the main compound, in addition to the olefins, and alkylidene.

04

[redacted]

Reaction of $RuCl_2$(p-cymene) + PNCNP

$RuCl_2$(p-cymene) (15mg), PNCNP (18mg) and NEt_3 (10mg) was warmed in ^tBuOH at 60°C. The NMR spectrum showed the formation of the olefins, alkylidene and new complexes. The mixture was warmed overnight at 60°C. There was 35% consumption of the ligand. Only small amount of the degradation ~~product~~ byproduct of the ligand at δ152 was observed.

$RuCl_2$(p-cymene) (15mg), PNCNP (18mg) and NEt_3 was warmed in toluene at 60°C. The NMR spectrum showed ~~the~~ the slow formation of the olefins and alkylidene and very little (trace) of the new compound. The mixture was left standing overnight at 60°C. The NMR spectrum showed 40% consumption of the ligand.

[redacted] Reaction of $RuCl_2(p\text{-cymene})$ + PHCNP.

A mixture of $RuCl_2(p\text{-cymene})$ (15mg), PHCNP (18mg) and NEt_3 (10mg) was warmed in toluene (0.6g) at 80°C. The NMR spectrum showed a gradual formation of the olefins, alkylidene and new (had) compounds. The reaction was 98% completed after 1 hour and 20 minutes.

[redacted] A mixture of $RuCl_2(p\text{-cymene})$ (13mg) PHCNPC (18mg) and NEt_3 (10mg) was heated at 80°C in ^tBuOH (0.6g). The NMR spectra showed gradual formation of the 4 main products. The reaction was 95% completed ~~at~~ in 2½ hours, however, there was some formation of the ligand degradation product at 81.52 (31P). The reaction mixture was allowed to stand at 60°C overnight, then filtered, the solids washed with methanol and redissolved on CD_2Cl_2. The NMR spectrum showed approximately 60% of the new complex along with the olefins, and alkylidene.

06

[redacted] Reaction of $RuCl_2$(p-cymene) + PNCNP.

A mixture of $RuCl_2$(p-cymene) (15 mg) PNCNP (18 mg) and NEt_3 (8 mg) was warmed at 80°C in iPrOH (no reaction at room temperature). The NMR spectrum showed the gradual formation of the various products along with a species at δ 112 (^{31}P) and δ -15.8 (^1H), which may be the dihydride. There was also a gradual formation of a green ppt, which coats the inside of the NMR tube.

[redacted] Reaction of $RuCl_2$(p-cymene) + PNCNP

Preparative reaction.

A mixture of $RuCl_2$(p-cymene) (1.3 g), PNCNP (1.8 g) and NEt_3 (0.56 g) [redacted] toluene (10 ml) was warmed for 1½ hour at 80°C. The NMR spectrum of the reaction mixture showed complete formation of the olefin isomers, alkylide and new compound. The solvent was reduced to ¼ in volume to 2 ml, during which there was a precipitation of an orange solid. This was filtered, washed with methanol and dried under vacuum. The mother liquor and washings was evaporated to dryness. 3 ml of methanol was added and the mixture stirred for 30 minutes. The solids were filtered, washed with

3 x 1 ml methanol and dried under vacuum. The combined yield = 1.844g.

A third crop (115mg) was obtained from the mother liquor which was left standing in the refrigerator (-15°C) for 1 week.
Combined total yield = 1.957g.

Reaction of RuHCl(PNNP) complexes with H_2
15 mg of the the mixture of complexes was dissolved in toluene-d8 (0.6g) in a Young NMR tube and the solution exposed to an atmosphere of H_2 gas. The NMR spectrum shows the clean formation of the dihydride complex.

The solution of the dihydride complex was exposed to Argon gas after 3 freeze-pump-thaw cycles. There was only a very slow conversion of the dihydride complex; only 10% change after 24 hours and 15% after 5 days.

Upon heating a suspension of the olefin and alkylidene RuHCl(PNNP) complexes in toluene-d8, a new complex (δ = 22.23 hydride region) constituted the main species. This new complex seems to be in equilibrium with the olefin and alkylidene complexes.

[redacted]

Sublimation of $RuHCl(PNNP)$ complexes. 100 mg of a mixture of the olefin and alkylidene complexes was sublimed under vacuum at 210°C. The NMR spectrum of the residue shows mainly the new compound (89%) along with the olefin and alkylidene complexes.

[redacted]

Exposure of a solution of the new compound to H_2 gas resulted in the formation of $RuH_2Cl(PNCNP)$.

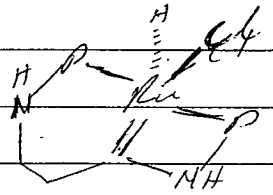
[redacted]

Preparation of $RuCl(CO)_2(PNCNP)$
A solution of the $RuHCl(PNNP)$ complexes (100 mg) was dissolved in 10 g of pyridine and the resulting solution stirred under an atmosphere of CO gas for 1 hour. The solvent was removed under vacuum, to give a tan-colored residue. yield = 108 mg.

Preparation of $RuCl(CO)(PNCNP)$
100 mg of the dicarbonyl complex was refluxed for 4 hours in toluene under argon. The solvent was then removed under vacuum, resulting in an orange residue. yield = 92 mg. ν_{CO} = 1899 cm^{-1}

[redacted]

The "new compound" was determined to be the fischer carbene complex:



[redacted]

Reaction of $RuH(N_2)(PCP)$ with H_2SiPh_2.

$PCP = {}^tBu_2P\sim\sim P{}^tBu_2$

H_2SiPh_2 (5mg) was added to a solution of $RuH(N_2)(PCP)$ (22mg) in C_6D_6 (0.6g). The NMR spectrum showed a mixture of products.

[redacted]

Reaction of $RuHCl(PCP)$ complex with PMe_3.

The mixture of olefin complexes (25mg) in C_6D_6 and PMe_3 (20mg) formed a clear solution as soon as it was prepared. The NMR spectrum showed the formation of $RuHCl(PMe_3)_4$.

Reaction of $RuHCl(PNNP)$ with PMe_3.

A mixture of the complexes (23mg) and PMe_3 (20mg) in C_6D_6 resulted in a clear solution instantaneously due to the formation of $RuHCl(PMe_3)_4$.

[redacted]

Reaction of $[Rh(cod)Cl]_2$ with PNCNP

A mixture of $[Rh(cod)Cl]_2$ (15mg), PNCNP (20mg) in 0.5g of C_6D_6 was prepared in an NMR tube. Two new species (^{31}P) were observed after 20 minutes at room temp.

The sample was heated for 20 minutes at 80°C under H_2 gas. A new species at 126.8 ppm (^{31}P) appeared.

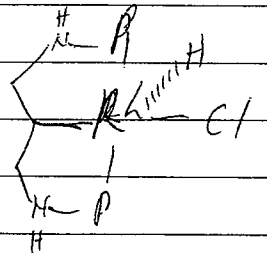
The sample was refluxed for 1 hour. The conc. of new complex increases with the formation of a bright yellow ppt.

[redacted]

The solvent was decanted (from above), the solid was dissolved in C_6D_6 (warm). Only one species present (NMR).

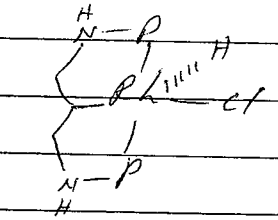
[redacted]

The reaction was repeated in iPrOH under H_2 gas. The solvent was decanted, the residue washed with (iPrOH, MeOH), dried and dissolved in C_6D_6. NMR showed same complex at 126.8 ppm (^{31}P).



Equilibrium reaction of RuHCl(PNCNP) species.
10 mg of a sample consisting mainly of the Fischer carbene complex (72%) was ~~was prepared~~ prepared by shaking in CD_2Cl_2 (0.8 g), filtering the solution and run the NMR. It consists of Fischer carbene (72.35%), anti olefin (13.47%), syn olefin (11.66%) and schrock carbene (2.52%). The solution was left standing at room temperature.
After 48 hours (13/11/02) the NMR showed Fischer carbene (36.49%), anti olefin (21.39%), syn olefin (40.26%) and schrock carbene (1.86%).

Preparation of



A mixture of $[Rh(cod)Cl]_2$ (150 mg) and PNCNP (250 mg) in 2-propanol (2 ml) was refluxed for 2 hours under H_2 gas. The mixture was cooled to room temp., filtered, the solids washed with 2-propanol (0.5 ml), MeOH (1.0 ml), and dried under vacuum.

yield = 282 mg.

[redacted]

Reaction of $[RuCl_2(p\text{-cymene})]_2$ with POP.

$PtBu_2$
= POP
$PtBu_2$

A mixture of $[RuCl_2(p\text{-cymene})]_2$ (15 mg) and POP (20 mg) was heated under H_2 gas in C_6D_6 (0.6 g) at 80°C overnight. The NMR spectrum showed extensive H-D incorporation in C_6D_6 (59% of CHD_3) and the presence of two major species (-13 ppm, (H_2) complex?) and -40 ppm.

[redacted]

Reaction of $RhHCl(PNCNP)$ with H_2SiPh_2

A mixture of $RhHCl(PNCNP)$ (2 mg) and H_2SiPh_2 (30 mg) [redacted] in C_6D_6 (0.6 g) was prepared. No reaction occured at room temperature. The mixture was heated to 60°C for 10 minutes. There was evolution of H_2. The NMR spectrum showed broadened peaks (polymerization?)

The experiment was repeated using 2 mg $RhHCl(PNCNP)$ and 30 mg H_2SiPh_2. The mixture was heated for 20 minutes at 60°C in C_6D_6 (0.6 g).

Email from Dmitri Zargarian

(1) mostly $PhHSiH_2$ (5.2 ppm)
(2) $(PhSiH_2)_2$ (4.5 ppm)
(3) some oligomerization and possible cyclic oligomers

[redacted]

A mixture of $[RuCl_2(p\text{-cymene})]_2$ (15 mg), POP (20 mg) and NEt_3 (5 mg) in 2-propanol (0.6 g) was heated at reflux for 12 hours. The NMR spectra showed the presence of several products.

[redacted]

Reaction of $[Ir(cod)Cl]_2$ with PNCNP

A mixture of $[Ir(cod)Cl]_2$ (20 mg), PNCNP (25 mg) in 2-propanol (0.6 g) was refluxed for 2 hours. The NMR spectrum showed the formation of one complex. (119 ppm (31P)).

[redacted]

Preparation of IrHCl(PNCNP)

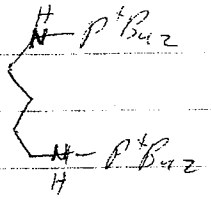
A mixture of $[IrCl(cod)]_2$ (200 mg) and PNCNP (250 mg) in 2-propanol (2 ml) was refluxed for 2 hours under Argon. The mixture was cooled, the solids filtered, washed with 2-propanol and MeOH and dried under vacuum.

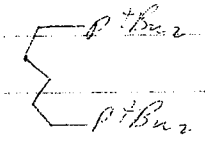
yield = 322 mg

The NMR spectra showed a mixture of IrHCl(PNCNP) (62%) and IrH_2(PNCNP) (38%)

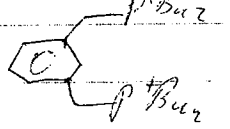
[redacted] Reaction of $Ir HCl(PNCND)$ with $H_3Si.Ph_2$

A mixture of 225 mg of $Ir HCl(PNCND)$ (from NMR reaction) and XS $H_3Si.Ph$ (8 mg) was prepared in C_6D_6 (0.6 g). The NMR spectrum showed the presence of 3 species.

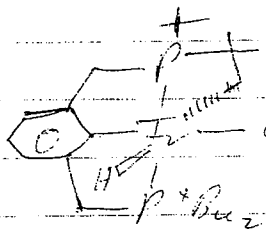
[redacted] Preparation of 

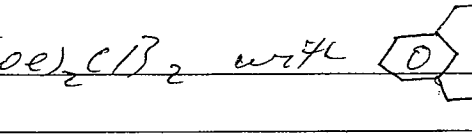
[redacted] Reaction of $[Ir(coe)_2Cl]_2$ with 

A mixture of $[Ir(coe)_2Cl]_2$ (20 mg) and the ligand (25 mg) in i-prOH (0.6 g) was refluxed for 30 minutes. The NMR spectrum showed the presence of $IrHCl(CPCP)$ (2 isomers) and $Ir H_2(PCP)$.

[redacted] Reaction of $[Ir(coe)_2Cl]_2$ with 

A mixture of $[Ir(coe)_2Cl]_2$ (18 mg) and the diphosphine (19 mg) was refluxed in 0.6 g 2-prOH for 4 hours, during which a orange solid precipitated. The solid was filtered, washed with 2-prOH and dried. It was dissolved in CD_2Cl_2 and the NMR obtained.

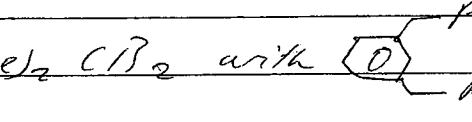
Product = based on NMR 

[redacted] Reaction of $[Ir(coe)_2Cl]_2$ with 

A mixture of $[Ir(coe)_2Cl]_2$ (19 mg) and the diphosphine (20mg) was prepared in toluene (0.6 g). The NMR spectrum showed the presence of ~~the~~ $HCl(PCP)$, $IrH_2(PCP)$ and two other species after standing under H_2 gas for 10 minutes.

The mixture was then degassed and left standing under Argon for 2 hours. The NMR spectrum showed the presence of the monohydride, dihydride and a new species (-26.76 ~~(br)~~ -37.3 ppm (br) in the hydride region.

A new sample was prepared and ~~refluxed~~ heated under H_2 gas in Toluene (80°C) for 10 minutes. The NMR spectrum showed mainly the monohydride and dihydride complexes.
No significant change after heating for 2 hours.

[redacted] Reaction of $[Ir(coe)_2Cl]_2$ with 

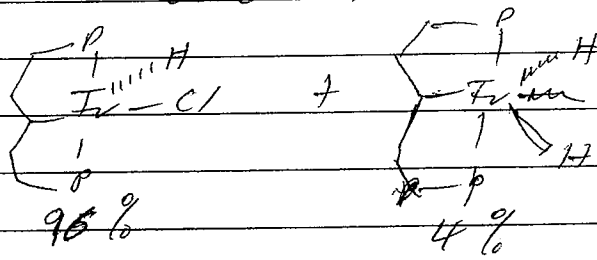
A mixture of $[Ir(coe)_2Cl]_2$ (20mg) and the diphosphine (25 mg) in 2-pentanol (0.6 g) was refluxed under H_2 gas for ~~24~~ 4 hours. The NMR spectrum showed 82 % formation of the monohydride and 18 % of a new species.
~~was detected~~

16

[redacted]

Reaction of $[Ir(coe)_2Cl]_2$ with P^tBu_2 / P^tBu_2

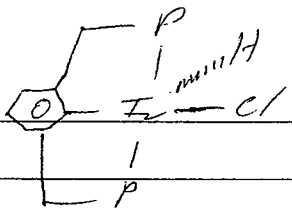
A mixture of ~~[illegible]~~ $[Ir(coe)_2Cl]_2$ (20mg) and the ligand (25mg) in 2-PrOH (0.6g) was refluxed under H_2 gas for 68 hours. The sample was cooled to R.T., decanted washed with 2-PrOH and dried. The NMR spectrum in C_6D_6 showed the presence of:



[redacted]

The experiment was repeated using $[Ir(cod)Cl]_2$ (20mg) and ligand (~~25~~mg) and refluxing in 2-pentanol for 3 days. It was cooled, decanted, washed with 2-PrOH and dried. The NMR spectrum showed the monohydride (90.5%), ~~and~~ ~~other~~ dihydride (1.81%) and 2 other species (3.89%) and (3.80%).

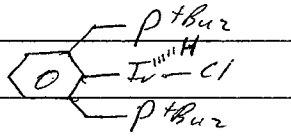
[redacted]

Preparation of 

A mixture of $[Ir(OE)_2Cl]_2$ (200 mg) [redacted] and the diphosphine (250 mg) in 2-pentanol (5 g) was refluxed under H_2 gas for 4 hours. The solids were filtered, washed with 2-propanol and dried under vacuum. The NMR spectrum showed the presence of the monohydride complex 82% and a dihydride species (18%). They were separated by [redacted] repeatedly decanting the [redacted] supernatant portions (containing dihydride) of a slurry of the mixture in 2-pentanol.

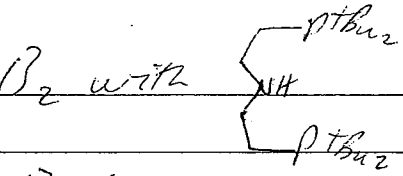
yield of monohydride = 220 mg
yield of dihydride = 116 mg.

[redacted]

Reaction of  with H_3SiPh.

A mixture of the monohydride complex (20mg) and H_3SiPh (50 mg) in C_6D_6 (0.6 g) was left standing overnight. The NMR spectrum showed the formation of a species in 83% (^{31}P) along with 4 minor species (7.6, 8.1, [redacted] and 5.4 %).

[redacted]

Reaction of $[Ir(coe)_2Cl]_2$ with 

A mixture of $[Ir(coe)_2Cl]_2$ (20 mg) and the ligand (25 mg) was refluxed for 30 minutes in 2-PrOH (0.6 g). A precipitate resulted. The supernatant was decanted, the solids washed with 2-PrOH and dried under vacuum. The NMR spectrum in CD_2Cl_2 showed the presence of 3 complexes (31P – 84%, 8%, 8%).

[redacted]

The above reaction was repeated using toluene and heating at 80°C for 20 minutes. The NMR spectrum showed the presence of 6 complexes (31P, 1.8%, 1.8%, 20.4%, 68.4%, 6.5%, 1.2%).

[redacted]

A mixture of $[Ir(coe)_2Cl]_2$ (22 mg) and the diphosphine (18 mg) was prepared in toluene (Room Temp). The NMR spectrum showed the formation of one main species (95%). Broad hydride signal (– 25.4 ppm).

[redacted] A mixture of $[Ir(CO)_2Cl]_2$ (20mg) and the PNHP ligand (20 mg) was refluxed in CH_2Cl_2 (0.6 g) for 8 hours. A colourless solid precipitated. The supernatant was decanted and the solid dissolved in CH_2Cl_2. The NMR spectrum showed the formation of one product as a mixture of isotopomers.

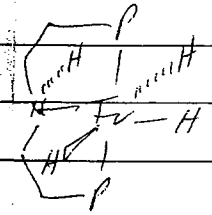
[redacted] Preparation of $IrHCl(PNP)(CO)$.

A mixture of $[Ir(CO)_2Cl]_2$ (0.0675 g) and the diphosphine PNHP (0.540g) was dissolved in 0.5 ml toluene and stirred for 20 minutes. A colourless ppt started to form and hexanes (10 ml) was added. The mixture was stirred for an additional 30 minutes. The solids were filtered, washed with hexanes, and dried under vacuum.

yield = 0.772 g.

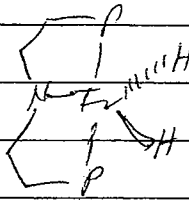
[redacted] Preparation of $IrH_3(PNHP)$

A mixture of $IrHCl(PNP)(CO)$ (100 mg) and $NaBH_4$ (30 mg) in EtOH (2 ml) was warmed at 60°C for 20 minutes. The colourless solids were filtered, washed with EtOH and dried under vacuum. The NMR spectrum in CH_2Cl_2 (insoluble in C_6D_6) showed the presence of $IrH_3(PNHP)$. Note - NaCl was not removed.



[redacted]

Preparation of $IrH_2(PNP)$



A mixture of $IrH_2(PNHP)$ (30 mg) in C_6D_6 (0.6 g) was refluxed under Argon, with degassing and refilling with Ar (3 times). The colourless solution changes to yellow. The NMR spectrum showed the clean formation of $IrH_2(PNP)$.

[redacted]

A mixture of $[Ir(coe)_2Cl]_2$ (30 mg) was ~~refluxed~~ heated (80°C) in toluene for 8 hours. The NMR spectrum showed the formation of only one complex as a mixture of isotopomers. Integrate for 1 hydride (?).

[redacted]

300 mg of Acetophenone; 10 mg of $IrH_2(PNHP)$ and 2.5 g of 2-propH was refluxed for 6 hours at 80°C. The NMR spectrum showed the formation of phenylethanol (80%!!).

[redacted]

The above ~~by~~ transfer hydrogenation was repeated. The NMR showed 86% conversion of the ketone to the alcohol.

[redacted] A mixture of 50 mg of acetophenone, 2.5 g 2-propanol and 10 mg of $IrH_2(PNHP)$ was refluxed (2 hours) in an open test tube (IN AIR). The NMR spectrum showed 98% conversion of the ketone to the alcohol.

[redacted] Preparation of $IrHCl(PNP)(CO)$

The complex was prepared using 2.09 g $[Ir(CO)_2Cl]_2$ (2.0 g) and PNHP (1.65 g).
Yield = 2.32 g.

[redacted] Preparation of $IrH_2(PNP)$.

150 mg of $IrH_2(PNHP)$ was sublimed under dynamic vacuum for 2 hours at 150°C.
Yield = 132 mg of the dihydride

[redacted] Ethanol (5 ml) was added to a mixture of $IrHCl(PNP)(CO)$ (1.2 g) and $NaBH_4$ (100 mg) and the mixture warmed for 20 minutes at 60°C. The solids were filtered, washed with ethanol and dried under vacuum. They were repeatedly extracted with 4 × 5 ml of CH_2Cl_2. The combined extracts was evaporated to dryness, under vacuum (refilling with H_2 if solution becomes yellow). Ethanol (2 ml was then added) and

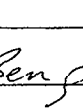
The mixture stirred for 20 minutes under nitrogen. The solids were filtered and dried under vacuum. Yield = 0.682g.

[redacted] Hydrogenation of cyclohexanone

A mixture of cyclohexanone (200 mg), 2-PrOH (2.5g) and $Ir H_3(PNHP)$ (5mg) was refluxed for 4 hours. The NMR spectrum showed 100% conversion of the ketone to the alcohol.

[redacted] Hydrogenation of 2-pentanone 

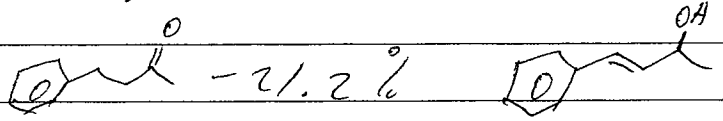
A mixture of 200 mg of the ketone, 2.5g of 2-PrOH and 5mg of $Ir H_3(PNHP)$ was refluxed for 4 hours under Argon. The NMR spectrum showed 100% conversion to the alcohol.

[redacted] Hydrogenation of Benzophenone 

200 mg ketone, 2.5g 2-PrOH, 5mg $Ir H_3(PNHP)$ reflux for 4 hours. 77% formation of the alcohol.

[redacted]

Hydrogenation of benzalacetone 
200 mg ketone, 2.3 g 2-proH, 5 mg $IrH_2(PNHP)$ reflux for 4 hours.
NMR spectrum showed 27.6% conversion.



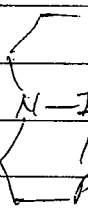
[redacted]

A mixture of $IrH_2(PNHP)$ (15 mg) and 2-proH (10 mg) was prepared in 2-proH (RT). The NMR spectrum showed no formation of $IrH_2(PNHP)$.
The mixture was heated for 2 hours at 80°C. No formation of $IrH_2(PNHP)$ was observed.

[redacted]

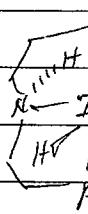
A mixture of $IrHCl(PNP)$ (ME) (25 mg) and 2-proH (10 mg) in C_6D_6 (0.6 g) was heated at 80°C for 40 minutes. Colourless ppt formed. The solvent was decanted, dried and the solids dissolved in CD_2Cl_2. The NMR spectrum showed one compound as a mixture of isotopomers.

[redacted]



A mixture of $IrHCl(PNP)(OEt)$ (250 mg), 2-propH (200 mg) in hexane (2 g) was refluxed for 1 hour, yielding a brick red solid. This was washed with hexanes and dried under vacuum. Yield = 192 mg.

[redacted]



Preparation trans-$IrH_2Cl(PNHP)$.
A solution of $IrHCl(PNP)$ (10 mg) in CD_2Cl_2 (0.8 g) was exposed to an atmosphere of H_2 gas. The NMR spectrum showed the formation of trans-$IrH_2Cl(PNHP)$.

[redacted]

Hydrogenation of Acetophenone.
1.0 g of Acetophenone, 3.0 g of 2-propH, 10 mg of KOMe and 10 mg of $IrH_2(PNHP)$ was refluxed at 80°C overnight. The NMR spectrum showed 82% conversion of the ketone to the alcohol.

[redacted]

Preparation of $[H(OEt_2)_2][BAR^F_4]$.

715 mg of $NaBAR^F_4$ and 1400 mg of 2M HCl solution in Et_2O and 1.5 ml of ether was stirred for 30 minutes. The ppted NaCl was removed by filtration and 15 ml of hexane added. Stirring with a spatula resulted in colourless crystals of the product. Yield = 715 mg.

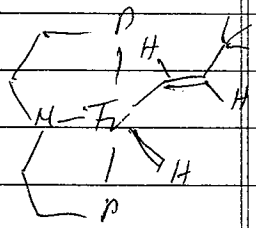
[redacted] Reaction of $IrH_2(PNP)$ with H_3SiPh.

30 mg of the dihydride and 6 mg of H_3SiPh in C_6D_6 (0.6 g) showed the clean formation of the 6-silane trihydride complex.

[redacted] Reaction of $IrH_2(PNHP)$ with H_3SiPh.
A mixture of the trihydride complex (5 mg) and H_3SiPh (3 mg) in C_6D_6 (0.6 g) showed the formation of 14% of the 6-silane complex.
42% after 4 days
80% after 1 week

[redacted] Reaction of $IrH_2(PNP)$ with H-C≡C-t

A mixture of $IrH_2(PNP)$ (20 mg) and xs alkyne (30 mg) was left standing for two days. The NMR spectrum showed the formation of vinyl complex.



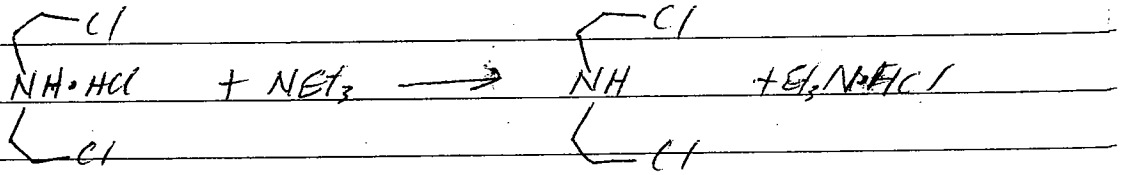
[redacted] Preparation of

28

[redacted]

mass of $\ce{NH(CH2CH2Cl)2}$ = 0.67g

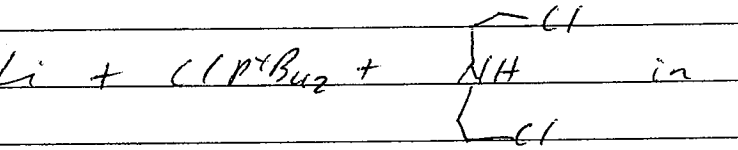
Preparation of $\ce{NH(CH2CH2Cl)2}$



1.5g of bis(chloroethyl)amine hydrochloride was warmed at 50°C for 24 hours in NEt_3 (5ml) with stirring. The mixture was filtered, the solids washed with 5ml of NEt_3, and the combined filtrate evaporated under vacuum. The remaining pale yellow liquid was distilled under vacuum at 50°C, yielding bis(chloroethyl)amine as a colourless liquid.

yield = 0.67g.

[redacted]



Lithium metal (0.45g) was added to a mixture of ClP^tBu_2 (2.74g) and bis(chloroethyl) amine (3.2g) in THF (15g) at −80°C. The mixture was stirred for 1 hour, then allowed to reach room temp (1 hour). The mixture was then stirred for an additional 4 hours at room temperature. The mixture showed a major peak at −21.2 ppm ($^31P\{^1H\}$).

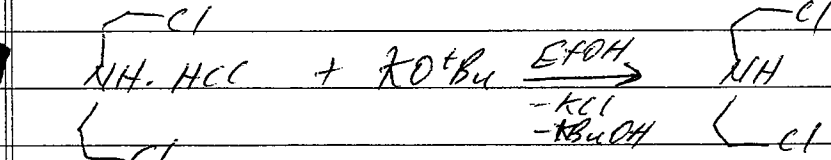
[redacted]

Preparation of LiP^tBu_2.

$ClP^tBu_2 + Li \xrightarrow{THF} LiP^tBu_2 + LiCl$

ClP^tBu_2 (14 g) was added in 2 ml portions to a vigorously stirred mixture of THF (140 ml) and lithium granules (1.5 g). The additional portions of ClP^tBu_2 was added only after the reaction mixture developed a distinct yellow colour (5–10 min) (Caution!! faster addition results in boiling and the mixture being thrown out of the flask). After addition was complete, the mixture was stirred at room temperature for 72 hours. The NMR spectrum showed 96% LiP^tBu_2.

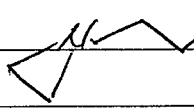
[redacted]



A mixture of bis(chloroethyl)amine hydrochloride (17.8 g) and KO^tBu (11.5 g) in EtOH (50 ml) was stirred at room temperature for 4 hours. The mixture was filtered and evaporated under reduced pressure. Yield of crude bis(chloroethyl)amine = 12.92 g. The crude amine was distilled at 50°C under vacuum yielding 11.52 g of pure bis(chloroethyl)amine.

[redacted] $ClP^tBu_2 + Li \xrightarrow{THF} LiP^tBu_2 + LiCl$

16 g of bis(chloroethyl)amine was added to the solution of LiP^tBu_2 in THF (from 04/02/03) at −80°C. The mixture was stirred at −80°C for 1 hour and allowed to reach room temperature slowly (≈ 2 hours). The mixture was then stirred for an additional 4 hours at room temperature, then refluxed (1 hour). It was then filtered, the THF removed under reduced pressure and the phosphine distilled. The fraction which boiled at 60°C under vacuum was collected. The NMR spectrum showed the aziridine (93%).



yield = 8.2 g.

[redacted] $ClPPh_2 + Li + THF \longrightarrow LiPPh_2 + LiCl$

$ClPPh_2$ (15.0 g) was added in 2 ml portions to a stirred suspension of Li granules (1.5 g) in THF (50 ml). (Caution!!) The resulting mixture was stirred for 72 hours at room temperature. The NMR spectrum showed 97% $LiPPh_2$.

[redacted]

Preparation of $N(CH_2CH_2Cl)_2SiMe_3$

$$NH(CH_2CH_2Cl)_2 \cdot HCl + ClSiMe_3 + NEt_3 \longrightarrow N(CH_2CH_2Cl)_2SiMe_3 + NEt_3 \cdot HCl$$

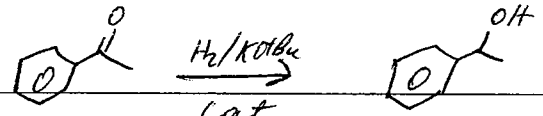
A mixture of bis(chloroethyl) amine hydrochloride (7.5g), Et_3N (100 ml) and $ClSiMe_3$ (4 ml) was heated to reflux for 12 hours. The mixture was cooled and filtered. The solids was washed with 50 ml Et_3N and the combined filtrate evaporated to give a yellow oil. This was diluted with hexane (25 ml) and the resulting mixture filtered. The solution was evaporated under vacuum to yield the product. It was stored in the refrigerator of the glove box.

yield = 26.82g.

[redacted]

$$LiPPh_2 + N(CH_2CH_2Cl)_2SiMe_3 \xrightarrow[-LiCl]{THF} N(CH_2CH_2PPh_2)_2SiMe_3 \xrightarrow[(2)\ HCl]{(1)\ H_2O} NH(CH_2CH_2PPh_2)_2 \cdot HCl$$

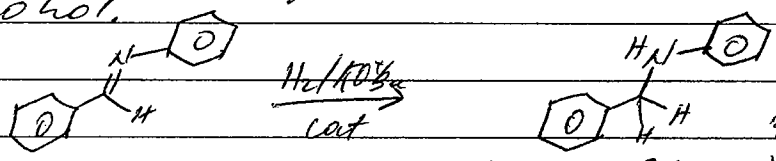
A solution of $(ClCH_2CH_2)_2NSiMe_3$ (8.5g) in THF (10 ml) was added to the mixture of $LiPPh_2$ (from 11/02/03) at $-40^\circ C$. The mixture was allowed to warm to room temp, stirred for 1 hour then refluxed for 1 hour. The white suspension was then cooled to R.T. and 15 ml of water added. It was stirred for 1 hour at room temp, the bottom (water)



1.0g

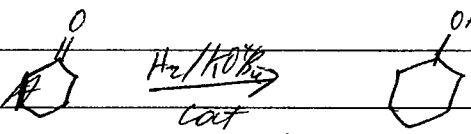
cat = $RuCl_2(Ph_2PC_2H_4)_2NH$

A mixture of acetophenone (1.0g), KO^{t}Bu (10mg) and catalyst (10mg) was stirred under H_2 gas (3atm) for 3 hours. The NMR spectrum showed 100% conversion of the ketone to the alcohol.



1.5g cat = $RuCl_2(Ph_2PC_2H_4)_2NH$

A mixture of the imine (1.5g), KO^{t}Bu (10mg) catalyst (10mg) was stirred under H_2 gas (3atm) for 1 hours. The NMR spectrum showed 100% conversion of the imine to the amine.



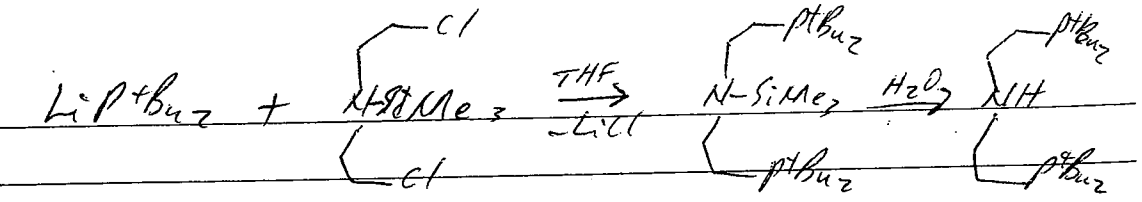
1.0g

cat = $RuCl_2(Ph_2PC_2H_4)_2NH$

A mixture of the ketone (1.0g), KO^{t}Bu (10mg) and catalyst (10mg) in 2-propanol was stirred under H_2 gas (3atm) for 3 hours. 100% conversion to the alcohol.

34

[redacted]



A solution of $(ClCH_2CH_2)_2NSiMe_3$ (9.0g) in THF (10ml) was added slowly to a solution of LiP^tBu_2 in THF (from 17/02/03) at -80°C. The mixture was then allowed to warm to room temperature and stirred for 1 hour. It was then refluxed for 1 hour. 15 ml of water was added after the mixture cooled to R.T. and stirred for 1 hour. The aqueous layer was removed and another 15 ml of H_2O added. The mixture was refluxed for 12 hours (with 20 ml of hexane). The aqueous layer was removed, and the mixture evaporated to dryness. It was then distilled under vacuum. The fraction boiling between 150-160°C was collected.

Yield = 12.22g.

[redacted]

$$ClP^iPr_2 + Li \xrightarrow{THF} LiCl + LiP^iPr_2$$

11.0g 1.5g

ClP^iPr_2 (11.0g) was added in 2g portions to a suspension of Li granules (1.5g) in THF (40ml) (Caution !!) The mixture was stirred for 3 days at room temperature.

[redacted] $[RuCl_2(C_6H_6)]_2$ + $(Ph_2P)_2NH\cdot HCl$ in pyridine – P

112mg 224mg 0.6g

Pyridine (0.6g) was added to a mixture of $[RuCl_2(C_6H_6)]_2$ and $(Ph_2P(C_2H_4)_2NH\cdot HCl$ (224mg).

[redacted] Preparation of $(ClC_2H_4)_2NSiMe_3$ – as per procedure.

[redacted] Preparation of $(iPr_2P)_2NH$

$$LiPiPr_2 + (ClC_2H_4)_2NSiMe_3 \xrightarrow[-LiCl]{THF} (iPr_2P)_2NSiMe_3 \xrightarrow{H_2O} (iPr_2P)_2NH$$

A solution of $(ClC_2H_4)_2NSiMe_3$ (7.75g) in 10 ml THF was added to a solution of $LiPiPr_2$ (from 22/02/03) at –80°C. The mixture was then allowed to warm to room temperature and refluxed for 1 hour. 15 ml of water was added and the mixture was stirred at R.T. for 1 hour. The aqueous layer was removed and 15ml of water and 15ml of hexanes added. The mixture was refluxed for 1 hours and the aqueous layer removed after cooling. The mixture was evaporated to dryness and distilled under vacuum. The fraction

36

[redacted] Preparation of LiP^tBu_2 – As per procedure

[redacted] Preparation of $HN(P^tBu_2)_2$ – As per procedure – Double distilled.

Yield = 12.56 g from 15g ClP^tBu_2

[redacted] $HN(PPh_2)_2 \cdot HCl$ + $[Ir(COE)_2Cl]_2$ + NEt_3 in C_6D_6

15 mg 12 mg 30 mg 0.6 g

Heat for 80°C for 10 minutes. Only 1 product formed (NMR).

[redacted] Reaction of $HN(PiPr_2)_2$ with $[Ir(COE)_2Cl]_2$

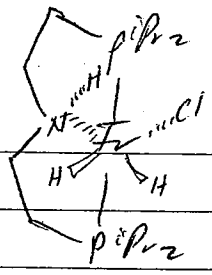
~~0.6g~~

0.6g 10 mg 11 mg

iPrOH R.T. – 1 product after 5 mins, 10 mins, 1 hr.
80°C for 10 minutes – main prod. = 89%

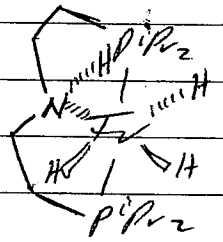
C_6D_6 R.T. – several products ~ 10 minutes.
80°C for 4 hours – several products

[redacted]

Preparation of 

2-propanol (3ml) was added to a mixture of $[Ir(COE)_2Cl]_2$ (1.5g) and $(^iPr_2PC_2H_4)_2NH$ (1.02g) and the mixture warmed for 45 minutes at 80°C. Hexanes (6 ml) was then added and the white precipitate filtered, washed with hexanes and dried under vacuum. Yield = 1052g.

[redacted]

Preparation of 

$IrH_2Cl((^iPr_2PC_2H_4)NH)$ + Superhydride in THF
20 mg 30mg @ 1.0M sol'n 0.6g
1 hour at R.T.

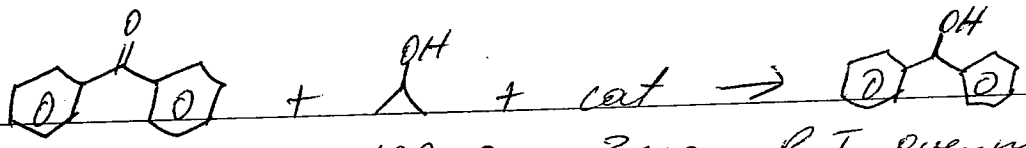
The NMR Spectrum showed the formation of $(IrH_2(^iPr_2PC_2H_4)NH)$ as the only product.

[redacted]

A mixture of $IrH_2Cl(PNHP)$ (800 mg) and Superhydride (1600 mg @ a 1M sol'n in THF) in THF (2 ml) was stirred for 12 hours at R.T. The mixture was evaporated to dryness and extracted with 3x10 ml toluene. The filtrate was evaporated to dryness, yielding the product as a viscous oil, which solidifies after 10 days. Yield = 628mg

40

[redacted]



30.09 100mg 3mg R.T. Overnight

S:C = 30,000 : 1 .

100 % conversion after slow evaporation.

KINETIC STUDY

using $Ir H_2(^iPr_2PC_2H_4)_2NH$.

Preparation of catalyst solution:

(1) 5 mg of catalyst was dissolved in 10 ml ^iPrOH.

(2) 2 ml of the solution was diluted to 10 ml in ^iPrOH.

(3) 0.5 g of the solution was mixed with 0.109 g Acetophenone and the mixture quickly equilibrated at the required temperature and the reaction monitored by ^1H NMR.

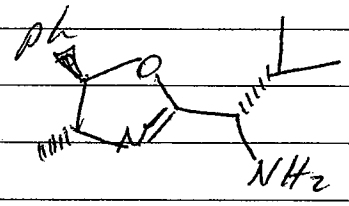
Final Substrate : catalyst ratio = 7200:1

25°C			40°C			50°C		
Time/min			Time/min			Time/min		
5	91.06	8.94	5	71.25	28.75	2	87.79	12.21
10	86.96	13.04	10	59.09	40.91	4	80.90	19.10
15	83.47	16.53	15	51.67	48.33	6	73.65	26.35
20	81.32	18.68	20	43.71	56.29	8	68.02	31.98
30	76.77	23.23	30	32.85	67.15	10	62.52	37.48
40	72.26	27.74	40	26.01	73.99	12	58.99	41.01
60	64.89	35.11	50	22.11	77.89	16	51.41	48.59
100	50.79	49.21				20	44.38	55.62
						30	34.55	65.45
						40	28.02	71.98

Kinetic study Cont'd

55°C			60°C			70°C		
Time/min			Time/min			Time/min		
2.5	68.13	31.87	2.5	68.66	31.35	2.5	80.16	19.84
4	59.65	40.35	4	54.92	45.08	4	62.17	37.83
6	50.67	49.33	6	45.29	54.71	6	56.09	43.91
8	40.01	59.99	8	38.30	61.70	8	51.43	48.57
10	33.33	66.67	10	32.80	67.20	10	46.21	53.79
12	29.22	70.78	12	29.17	70.83	12	42.14	57.86
16	23.23	76.77	16	23.77	76.23	16	31.88	68.12
20	21.65	78.35	20	21.11	78.89	18	29.13	70.87
30	19.41	80.59				22	25.23	74.77

[redacted]

Preparation of 

Oxam

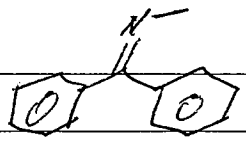
The oxazoline amine was prepared as illustrated in the literature by Sigman et al. – Organic Letters, 2002. The ligand was used for the preparation of ruthenium complexes without further purification.

[redacted]

Preparation of $RuHCl(PPh_3)_2(Oxam)$

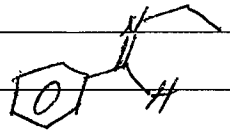
Toluene (5 ml) was added to a mixture of $RuHCl(PPh_3)_3$ (30 mg) and enough oxam to change the colour to a green solution. This solution was used for reactions.

[redacted]

Preparation of 

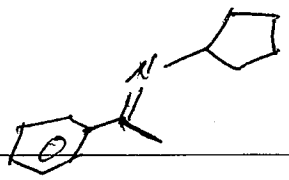
A mixture of benzophenone (3 g) and 2M methylamine solution in THF (100 ml) was refluxed over activated molecular sieves for 24 hours in a pressure flask. The mixture was then refluxed for an additional 48 hours after an additional 100 ml of the methylamine solution was added. The solvent and excess reagent was removed under vacuum. Yield = 4.8 g.

[redacted]

Preparation of 

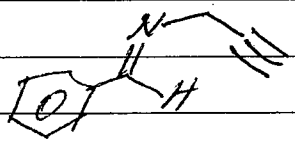
A mixture of benzaldehyde (10 g) and 2M ethylamine solution in THF 200 ml was stirred over activated molecular sieves for 12 hours. The mixture was ~~filtered~~ softened and the solvent and excess reagents removed under vacuum. Yield = 8.2 g

[redacted]

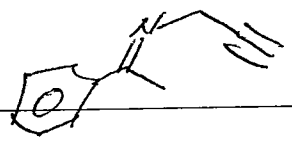
Preparation of 

A mixture of acetophenone (10g) and cyclopentylamine (15g) ~~in~~ toluene (30 ml) was refluxed for 48 hours over activated molecular sieves. The mixture was filtered, and the solvent and excess reagents removed under vacuum. The product was purified by distillation under vacuum. Yield = 7.2g.

[redacted]

Preparation of 

A mixture of benzaldehyde (10g) and propargyl amine (10g) in THF (50ml) was stirred over activated molecular sieves for 12 hours. The solvent was removed and the excess reagents was removed under vacuum. Yield = 7.0g.

[redacted] Preparation of 

A mixture of acetophenone (5g) and propargylamine (10g) in toluene (25ml) was refluxed for 48 hours over activated molecular sieves. The solvents and excess reagents were removed under vacuum.
Yield = 3.7g.

[redacted] Preparation of $RuHCl(PPh_3)_3$.

Toluene (100 ml) was added to $RuCl_2(PPh_3)_3$ (6g), followed by NEt_3 (2g). The mixture was flushed with argon gas, then flushed with hydrogen gas on a Schlenk line and refluxed for 12 hours under hydrogen gas. The mixture was allowed to cool to room temperature and stirred overnight. It was then filtered, washed with ethanol (3x 20 ml) then ether and dried under vacuum. Yield = 4.72g.

[redacted]

Preparation of RuHCl(Binap)(PPh_3)

THF (20 ml) was added to a mixture of $RuHCl(PPh_3)_3$ (1.5 g) and R-binap (1.1 g). The mixture was refluxed for 12 hours under argon. The solvent was then removed under vacuum. The solids were extracted with 3 x 20 ml of diethyl ether and the combined filtrate was concentrated to 5 ml. Hexanes (25 ml) was added to precipitate the red-orange product.
yield = 1.39 g.

[redacted]

Preparation of R,R-Dppach

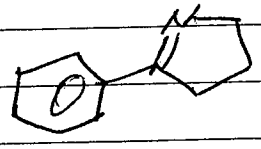
A solution of chlorodiphenylphosphine (3.83 g) dissolved in toluene (20 ml) was added dropwise to a solution of R,R-cyclohexyldiamine (1.0 g) and triethylamine (1.8 g) in toluene (20 ml). The mixture was then stirred for 6 hours under argon. It was then filtered, the solids washed with toluene, and the combined filtrate concentrated to 5 ml by evaporation under vacuum. Hexanes (30 ml) was then added, precipitating a white solid. This was filtered, washed with hexanes and dried under vacuum. Yield = 4.03 g.

[redacted]

Preparation of RuHCl(dppach)(pph3)

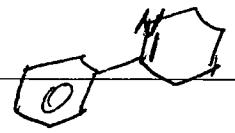
THF (10 ml) was added to a mixture of RuHCl(pph3) (1.5g) and dppach (0.85g) and the resulting mixture was refluxed for 4 hours under argon. The mixture was filtered and concentrated to 5 ml under vacuum. 20 ml of hexanes was then added and the mixture stirred for 4 hours under argon. A brick red product precipitated. This was filtered, washed with hexanes and dried under vacuum. Yield = 1.29g.

[redacted]

preparation of 

This was prepared using the procedure outlined by Sagi et al. JACS 1990, 112, 3567-79 and Kirsch et al. Tet. Lett. 2001, 42, 6101-04.

Kirsch method better, 92% yield!!

[redacted] Preparation of 

This was prepared as outlined in Gallulo et al. Org. prep. proc. Int. 1989, 21, 297.

[redacted] Preparation of RuHCl(R-binap)(R,R-cydn)

THF (2 ml) was added to a mixture of RuHCl(R-binap)(Pph3) (300 mg) and (R,R-cydn (40 mg) and the solution stirred for 1 hour under argon. The mixture was filtered and hexanes (15 ml) added, precipitating a bright yellow solid. Yield = 235 mg.

[redacted] Preparation of RuHCl(R-binap)(R,R-dpen)

300 mg of RuHCl(R-binap)(Pph3) and 60 mg of R,R-dpen were dissolved in 1 ml of THF and the mixture stirred for 30 minutes. The solution was filtered and hexanes (10 ml) added to the filtrate, precipitating a yellow solid. Yield = 261 mg.

[redacted] Preparation of RuHCl(R,R-dppach)(PPh3)

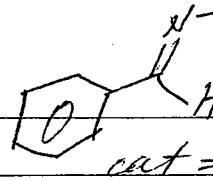
THF (2ml) was added to a mixture of 300 mg RuHCl(R,R-dppach)(PPh3) and 35 mg of R,R-cydn. The mixture was stirred for 1 hour under argon. It was filtered and 10 ml of hexanes added, precipitating a yellow-green solid. Yield = 236 mg.

[redacted] Preparation of RuHCl(R,R-dppach)(R,R-dpen)

300 mg of RuHCl(R,R-dppach)(PPh3) and 66 mg R,R-dpen were added to 1ml of THF and the mixture stirred for 30 minutes. The mixture was filtered and hexanes (10 ml) was added, precipitating an orange-red solid. Yield = 274 mg.

[redacted] Preparation of RuCl(R,R-dppach)(Cl-cat)

Toluene (5 ml) was added to a mixture of RuHCl(R,R-dppach)(PPh3) (100 mg) and enough chloranil to change the colour to a bright yellow-green. This solution was used as a catalyst stock solution

[redacted] Hydrogenation of 

cat = RuHCl(R-binap)(R,R-cydn)

0.68 g of the imine was dissolved in deuterated benzene (2 ml) and added to a 50 ml bomb reactor containing RuHCl(R-binap)(R,R-cydn) (5 mg) and KO^{t}Bu (10 mg) under Hydrogen gas. The reactor was pressurized to 15 bar and stirred for 24 hours at room temperature. The NMR spectrum of the reaction mixture showed complete conversion to the amine

[redacted] cat = RuHCl(R-binap)(R,R-dpen).

H_2 = 15 bar, Imine = 0.61 g, cat = 5 mg, KO^{t}Bu = 10 mg.

The reaction was setup as above NMR showed 100% conversion after 24 hours.

[redacted] cat = RuHCl(R,R-dppach)(R,R-cydn)

H_2 = 15 bar, Imine = 0.81 g, cat = 5 mg, KO^{t}Bu = 10 mg.

As above. Yield = 100% amine (NMR).

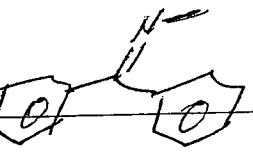
[redacted] Cat = RuHCl(R,R-dppach)(R,R-dpen)

Imine = 0.71 g, cat = 5 mg, KO^{t}Bu = 10 mg

H_2 = 15 bar. As above

NMR showed 100% conversion to amine.

[redacted]

Hydrogenation of 

A mixture of the imine (0.56g) in C_6D_6 (2 mL), catalyst (RuHCl(R-binap)(R,R-cydn), 5 mg) and KO^{t}Bu (10 mg) [redacted] in a Parr pressure reactor was stirred under hydrogen (30 bar) for 24 hours. The NMR of the reaction mixture showed complete conversion of the imine to the amine.

[redacted]

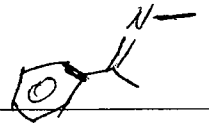
Cat = RuHCl(R-binap)(R,R-dpen)
Cat = 5 mg, imine = 0.50 g, KO^{t}Bu = 10 mg,
H_2 = 30 bar. Reaction as above.
NMR showed complete conversion of the imine to amine.

[redacted]

Cat = RuHCl(R,R-dppach)(R,R-cydn)
Cat = 5 mg, imine = 0.67 g, KO^{t}Bu = 10 mg
H_2 = 30 bar.
NMR = 100% conversion.

[redacted]

Cat = RuHCl(R,R-dppach)(R,R-dpen)
Cat = 5 mg, imine = 0.59 g, KO^{t}Bu = 10 mg
H_2 = 30 bar.
NMR showed 100% conversion.

[redacted] Hydrogenation of 

cat = RuHCl(R-binap)(R,R-cydn)

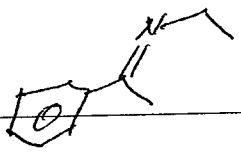
A mixture of the imine (0.459), catalyst (5mg) and KOtBu (10mg) ~~was~~ in C6D6 (2ml) was stirred under H2 gas (30 bar) for 24 hours at room temperature. The NMR spectrum showed 98% conversion of the imine.
α_D (c=2, chloroform) = −44.6°

[redacted] Cat = RuHCl(R-binap)(R,R-~~dpen~~cydn)
Cat = 5mg, Imine = 0.419, KOtBu = 10mg
H_2 = 30 bar.
NMR showed ~~99%~~ 97% conversion.
α_D = −51.1°.

[redacted] Cat = RuHCl(R,R-dppach)(R,R-cydn)
Cat = 5mg, Imine = 0.549, KOtBu = 10mg,
H_2 = 30 bar.
NMR showed 100% conversion of the imine to amine.
α_D = −34.6°.

[redacted] Cat = RuHCl(R,R-dppach)(R,R-dpen)
Cat = 5mg, Imine = 0.489, KOtBu = 10mg.
H_2 = 30 bar.
100% Conversion to amine.
α_D = −36.7°.

54

[redacted] Hydrogenation of 

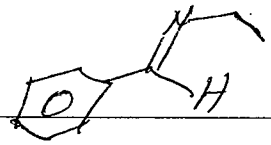
Cat = RuHCl(R-binap)(RR-cydn), H_2 = 30 bar
A mixture of the catalyst (5mg), KO^{t}Bu (10 mg), Imine (0.429) in C_6D_6 (2 ml) was stirred for 36 hours at room temperature. The NMR spectrum showed 95% conversion.

[redacted] Cat = RuHCl(R-binap)(R,R-dpen)
Cat = 5mg, Imine = 0.38g, KO^{t}Bu = 10mg
H_2 = 30 bar.
NMR showed 98% conversion.

[redacted] Cat = RuHCl(RR-dppach)(R,R-cydn)
Cat = 5mg, Imine = 0.5g, KO^{t}Bu = 10mg,
H_2 = 30 bar.
100 % conversion after 24 hours

[redacted] Cat = RuHCl(R,R-dppach)(R,R-dpen)
Cat = 5mg, Imine = 0.44g, KO^{t}Bu = 10mg
H_2 = 30 bar.
NMR showed complete conversion after 24 hours.

[redacted]

Hydrogenation of 

Catalyst = RuHCl(R-binap)(R,R-cydn).
A mixture of the catalyst (5mg), KO^{t}Bu (10mg), Imine (0.459) in C$_6$D$_6$ (2ml) was stirred under hydrogen gas (15bar) for 24 hours.
The NMR showed 100% conv.

[redacted]

Cat = RuHCl(R-binap)(R,R-dpen).
Cat = 5mg, Imine = 0.149, KO^{t}Bu = 10mg
H_2 = 15 bar.
Complete conversion in 24 hours.

[redacted]

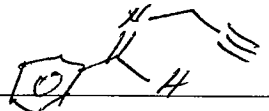
Cat = RuHCl(R,R-dppach)(R,R-cydn)

Cat = 5mg, Imine = 0.549, KO^{t}Bu = 10mg
H_2 = 15 bar.
100% conversion in 24 hours.

[redacted]

Cat = RuHCl(R,R-dppach)(R,R-dpen)

Cat = 5mg, Imine = 0.489, KO^{t}Bu = 10mg
H_2 = 15 bar.
Complete conversion in 24 hours.

[redacted] Hydrogenation of 

cat = RuHCl(R-binap)(R,R-cydn)

A mixture of the catalyst (3mg), KO^{t}Bu (10mg) and Imine (0.82g) was stirred for 24 hours under H_2 gas (15 bar). The NMR showed 100% conversion.

) in C$_6$D$_6$ (2ml)

[redacted]

cat = RuHCl(R-binap)(R,R-dpen)
cat = 5 mg, Imine = 0.73g, KO^{t}Bu = 10mg
H_2 = 15 bar.
100% Conversion in 24 hours.

[redacted]

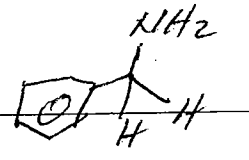
cat = RuHCl(R,R-dppach)(R,R-cydn)
cat = 5 mg, Imine = 0.98g, KO^{t}Bu = 10mg
H_2 = 15 bar.
Complete conversion in 24 hours.

[redacted]

cat = RuHCl(R,R-dppach)(R,R-dpen)
cat = 5 mg, Imine = 0.86g, KO^{t}Bu = 10mg
H_2 = 15 bar.
Complete conversion in 24 hours.

53

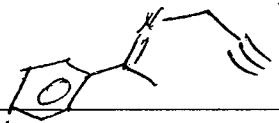
[redacted]

Preparation of 

The propargylamine prepared from reduction of the imine was used. The procedure follows the one reported by Banerji et al. (Tetahedron Lett. 1999, 40, 767-770).

A mixture of $TiCl_4$ (1.54 g) and lithium metal (231 mg) was refluxed for 3 hours under argon in THF (20 ml). A solution of the propargylamine (500 mg) in THF (5 ml) was added to the reagent and stirred for 1 hour at room temperature. The reaction mixture was diluted with hexane/ethyl acetate (70/30) and filtered through celite. The filtrate was washed with brine, dried (Na_2SO_4) and concentrated under vacuum. The crude product was purified by chromatography to yield benzylamine (245 mg).

[redacted]

Hydrogenation of 

cat = RuHCl(R-binap)(R,R-cydn)

A mixture of the catalyst (5mg), KO^{t}Bu (10mg) and imine (0.89g) in C_6D_6 (2mL) was stirred under H_2 gas (30 bar) for 24 hours. NMR showed 97% conversion.
e.e. = 78% (S)

[redacted]

cat = RuHCl(R-binap)(R,R-dpen)
cat = 5mg, Imine = 0.80g, KO^{t}Bu = 10mg
H_2 = 30 bar.
NMR showed 100% conversion.
e.e. = 67% (S)

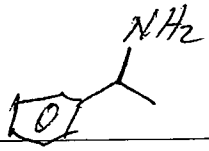
[redacted]

Cat. = RuHCl(R,R-dpppath)(R,R-cydn)
cat = 5mg, Imine = 1.07g, KO^{t}Bu = 10mg
H_2 = 30 bar.
100% Conversion. e.e. = 52% (S)

[redacted]

Cat. = RuHCl(R,R-dpppath)(R,R-dpen)
Cat = 5mg, Imine = 0.94g, KO^{t}Bu = 10mg
H_2 = 30 bar.
NMR showed 100% conversion.
e.e. = 51% (S).

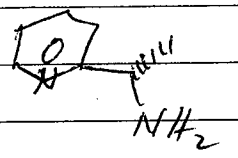
[redacted]

Preparation of 

Prepared from propargylamine derived from hydrogenation of imine. (Banerji et al, Tetrahedron Lett. 1999, 40, 767-770).

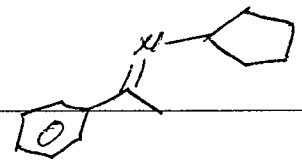
A solution of the propargylamine (500mg) was added to the LVT reagent and the resulting mixture was stirred for 2 hours at room temperature. The reaction mixture was diluted with hexanes/ethyl acetate (70/30) and filtered through celite. The crude product was purified using chromatography to yield the amine. Yield = 290mg.

[redacted]

Preparation of  S-MeAmpy

The ligand was prepared using the reported literature procedure Inorg. Synth. 1998, 32, 70.

[redacted]

Hydrogenation of 

Cat = RuHCl(R-binap)(R,R-cydn)

A mixture of the catalyst (5mg), ~~[illegible]~~ ~~[illegible]~~ Imine (0.219), KOtBu (20 mg) in C6D6 (2ml) was stirred under hydrogen (50 bar) for 36 hours. The NMR showed 90% Conversion of the imine to amine.

[redacted]

Cat. = RuHCl(R-binap)(R,R-dpen)
Cat = 5mg, Imine = 0.199, KOtBu = 20mg.
H_2 = 50 bar.
The NMR showed 83% Conversion after 36 hours.

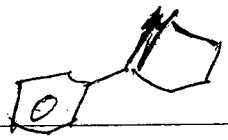
[redacted]

cat = RuHCl(R,R-dppach)(R,R-cydn)
cat = 5mg, Imine = 0.259, KOtBu = 20mg
H_2 = 50 bar.
97% Conversion in 36 hours.

[redacted]

cat = RuHCl(R,R-dppach)(R,R-dpen)
cat = 5mg, Imine = 0.229, KOtBu = 20mg
H_2 = 50 bar.
95% Conversion on 36 hours.

[redacted]

Hydrogenation of 

Cat = RuHCl(R-binap)(R,R-cydn)

Cat = 5mg, Imine = 0.16g, KO^{t}Bu = 30mg
H_2 = 50bar, C_6D_6 = 2ml.
92% conversion in 36 hours.

[redacted]

Cat = RuHCl(R-binap)(R,R-dpen)
Cat = 5mg, Imine = 0.15g, KO^{t}Bu = 30mg
H_2 = 50bar, C_6D_6 = 2ml.
89% conversion in 36 hours.

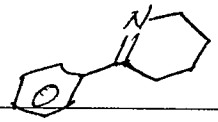
[redacted]

Cat = RuHCl(R,R-dppach)(R,R-cydn)
Cat = 5mg, Imine = 0.20g, KO^{t}Bu = 30mg
H_2 = 50bar, C_6D_6 = 2ml.
97% conversion in 24 hours.

[redacted]

Cat = RuHCl(R,R-dppach)(R,R-dpen)
Cat = 5mg, Imine = 0.17g, KO^{t}Bu = 30mg
H_2 = 50bar, C_6D_6 = 2ml.
93% conversion in 24 hours.

[redacted]

Hydrogenation of 

Cat = RuHCl(R-binap)(R,R-cydn)
cat = 3mg, Imine = 0.[redacted]g, tOBu = 20mg
H2 = 30 bar, C6D6 = 2ml.
82% conversion in 36 hours.

[redacted]

Cat = RuHCl(R-binap)(R,R-dpen)
cat = 3mg, Imine = 0.16 g, tOBu = 20mg
H2 = 50 bar, C6D6 = 2ml
76% Conversion in 36 hours.

[redacted]

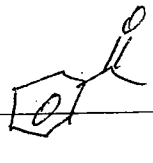
Cat = RuHCl(R,R-dppach)(R,R-cydn)
cat = 3mg, Imine = 0.22g, tOBu = 20mg
H2 = 50 bar, C6D6 = 2ml.
94% conversion in 36 hours.

[redacted]

Cat = RuHCl(R,R-dppach)(R,R-dpen)

Cat = 3mg, Imine = 0.19g, tOBu = 20mg
H2 = 50 bar, C6D6 = 2ml.
88 Conversion in 36 hours.

[redacted]

Hydrogenation of 

catalyst = RuHCl(R-binap)(oxam)

A mixture of the catalyst (5mg), KOtBu (10mg) and acetophenone (1.0g) in C_6D_6 was stirred for 24 hours under hydrogen (10 bar). TLC NMR showed 100% conversion to the alcohol (e.e. = 70% (S)).

[redacted]

cat = $RuHCl(PPh_3)_2$(oxam)

cat = 5mg, KOtBu = 10mg, C_6D_6 = 2ml, H_2 = 10 bar, acetophenone = 1.0g.

100% conversion in 24 hours.

[redacted]

cat = RuHCl(R,R-dppach)(oxam)

cat = 5mg, KOtBu = 10mg, acetophenone = 1.0g, H_2 = 10 bar

100% conversion in 24 hours.

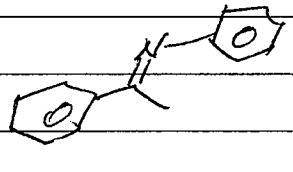
[redacted]

Hydrogenation of 

Three test tubes were used for the simultaneous hydrogenation of benzalacetone. Each tube contains (1) 5mg catalyst (2) 1g acetophenone (3) 10 mg KOtBu (4) 2ml C_6D_6. The tubes were placed in a Parr reactor and a magnetic stirrer placed on each. The pressure (H_2) was adjusted to 10 bar and stirred for 24 hours.

RuCl(pph3)(oxam) – 100%
RuHCl(R-binap)(oxam) – 100%
RuHCl(R,R-dppach)(oxam) – 100%

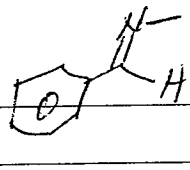
[redacted]

Hydrogenation of 

Test tubes were used for simultaneous hydrogenation. – (1) 10 mg catalyst (2) 10mg KOtBu (3) 0.5g imine (4) 2ml C_6D_6. pressure = 30 bar (H_2).
The mixtures were stirred for 24 hours.

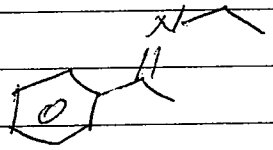
RuHCl(pph3)(oxam) – 87%
RuHCl(R-binap)(oxam) – 100%
RuHCl(R,R-dppach)(oxam) – 100%

[redacted]

Hydrogenation of 

Test tubes were used for simultaneous reactions. Each contained: (1) 10 mg cat. (2) 0.5 g imine (3) 10 mg KO^{t}Bu (4) C_6D_6 - ml. H_2 = 10 bar. The mixtures were stirred for 24 hours.

RuHCl(PPh_3)$_2$(oxam) - 88 %
RuHCl (R-binap)(oxam) - 100 %
RuHCl (R,R-dppach)(oxam - 100 %.

Hydrogenation of 

Each Test tube contained: (1) 10 mg cat. (2) 0.5 g imine (3) KO^{t}Bu = 20 mg (4) C_6D_6 = 2 ml. H_2 = 30 bar. After 36 hours:
RuHCl(PPh_3)$_2$(oxam) = 22 %
RuHCl (R-binap)(oxam) = 18 %
RuHCl (R,R-dppach)(oxam) = 27 %.

[redacted]

Preparation of Cl~~N(TMS)$_2$

NEt_3 (400 ml) was added to a mixture of 2-chloroethylamine hydrochloride (100g) in CH_2Cl_2 (1.5L) and the mixture stirred vigorously for 2 hours under argon. A solution of TMSCl (240 ml) in CH_2Cl_2 (400 ml) was then added slowly and the resulting mixture stirred vigorously at room temperature for 12 hours. The mixture was filtered, and the solids washed with 800 ml of CH_2Cl_2. The combined filtrate was evaporated to remove the solvents and hexane (500 ml) added. The mixture was stirred for 2 hours, then filtered, and the filtrate evaporated under reduced pressure to give the product as a pale yellow liquid. yield = 198.3g.

[redacted]

Preparation of $RuHCl(PPh_3)_2$(S-MeAmpy)

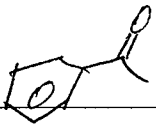
THF (5ml) was added to a mixture of $RuHCl(PPh_3)_3$ (200 mg) and S-MeAmpy (80 mg) and the resulting solution was stirred for 2 hours under argon. Hexanes (20 ml) was added and the yellow-green solid was filtered, washed with hexanes and dried under vacuum. yield = 152 mg.

[redacted]

Preparation of Ph_2P–NH_2

A THF (120 ml) solution of chlorodiphenylphosphine (60 g) was added slowly to a suspension of lithium granules (6.0 g) in THF (100 ml) and the mixture stirred for 3 days at room temperature. The mixture was filtered through a sintered glass frit to remove excess lithium and the filtrate cooled to −40°C. A solution of N,N-bis(trimethylsilyl)ethylamine (62 g) in 200 ml THF was slowly added. The resulting suspension was warmed to R.T. and the mixture was refluxed for 1 hour. After cooling to R.T. 50 ml of water was added. The mixture was refluxed for one hour, cooled to R.T. and the aqueous layer was removed. Another 50 ml of water and 50 ml of hexanes was added and the mixture was refluxed for 4 hours, the cooled to R.T. The aqueous layer was removed and the mixture was evaporated to give the crude aminophosphine. This was purified by vacuum distillation. Yield = 38.2 g.

[redacted]

Hydrogenation of 

if test tubes were used to simultaneously hydrogenate acetophenone under the same conditions using 4 amino pyridine catalysts. Each tube contained:

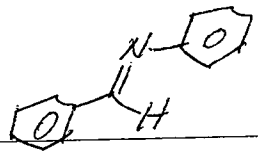
Cat = 5mg, KO^{t}Bu = 10 mg, Acetophenone - 1.0g, C_6D_6 = 2 ml

The tubes were placed in a Parr pressure reactor (10 bar) and stirred for 12 hours.

RuHCl(PPh_3)$_2$(S-MeAmpy) - 100%, 47% (R)
RuHCl(PPh_3)$_2$(Aepy) - 100%
RuHCl(S-binap)(S-MeAmpy) - 100%, 72% (R)
RuHCl(S,S-dppach)(S-MeAmpy) 100%, 59% (R)

70

[redacted]

Hydrogenation of 

Reactions were done in 4 test tubes.
① Cat = 5mg, Imine = 0.5g, KOtBu = 10mg
C_6D_6 = 2ml, H_2 = 10 bar.
Reaction mixtures were stirred for 24 hours.

RuHCl(pph3)(S-MeAmpy) – 100%
RuHCl(pph3)(Acpy) – 100%
RuHCl(S-binap)(S-MeAmpy) – 79%
RuHCl(S,S-dppach)(S-MeAmpy) – 100%